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Preparation of poly(3,4-ethylenedioxythiophene) (PEDOT) coated silica core–shell particles and PEDOT hollow particles

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Nanometre-sized PEDOT-silica core–shell particles were synthesized and self-assembled into crystalline colloidal arrays with a reflection peak in the visible region; these particles were also etched with hydrofluoric acid to produce hollow PEDOT particles.

The synthesis of colloidal particles with a core–shell morphology is attracting greater interest from researchers due to the diverse applicability of these particles as building blocks for the creation of photonic crystals, multi-enzyme biocatalysis, and as drug delivery systems.[1] The properties of colloidal spheres can be altered by coating the particles with an outer shell that influences the final optical, electrical, thermal, mechanical, magnetic, or catalytic properties. In general, the exploitation of a core–shell topology results in particles which exhibit properties that are unique to both the underlying core and shell.[2] The formation of the corresponding hollow shell architectures from these core–shell systems is also of interest for a number of purposes, *e.g.* producing photonic crystals, as delivery vehicle systems, catalysts, or highly porous materials.[3] Recently, there have been reports on the fabrication of hollow capsules based on the intrinsically conductive polymers polyaniline[4] and polypyrrole,[5] but as of yet, there have been no reports on the synthesis of hollow structures utilizing poly(3,4-ethylenedioxythiophene) (PEDOT). This is in part due to the intrinsic difficulty in generating colloidal particles based on this polymer, as evidenced by the scarcity of literature to this end.[6,7] PEDOT is one of the most promising conducting polymers due to its high environmental stability, low band gap, high conductivity, and excellent transparency in its doped state.[8]

In regard to self-assembled structures with a periodic dielectric modulation, researchers have utilized core–shell particles and their corresponding hollow particles in an attempt to enhance the photonic band gap through an increase of the refractive index contrast within the assembly.[9] To this end, our group has focused on the synthesis of intrinsically conducting polymer coated core–shell particles. Armes and coworkers first reported on the synthesis of micrometre-sized PEDOT-coated polystyrene particles,[6] while our group has recently prepared a similar system based on nanometre-sized particles.[10] These PEDOT coated polystyrene core–shell particles were self-assembled into a periodic structure which exhibited a stop band in the visible region. In this communication, we describe the first successful fabrication of a nanometre-sized PEDOT-coated silica core–shell particle and the self-assembly of these particles into a electrostatically stabilized 3D periodic structure. In addition, etching of the particles with a hydrofluoric acid (HF) solution removes the silica core, producing hollow PEDOT particles.

In a typical synthesis run, 3,4-ethylenedioxythiophene (EDOT) monomer (0.108 g) was first dissolved in a diluted colloidal silica solution with a diameter of *ca.* 130 nm (SNOWTEX ZL (NISSAN Chemical) 0.75 g of silica). Because the EDOT monomer is only slightly soluble in water and exhibits too high an oxidation potential to make it easy to polymerize, the solubility of EDOT in the dispersion medium was controlled by mixing methanol with deionized water and/or by using *p*-toluenesulfonic acid (*p*-TSA). This acid is known as a good dopant for PEDOT and confers an increased solubility of EDOT in water, possibly due to the enhanced protonation of EDOT.[7b] The EDOT adsorbs to the surface of the colloidal silica, where polymerization is initiated by the addition of 0.452 g of the oxidant ammonium persulfate (APS) to the stirred solution. After 20 h of polymerization at 30 °C, the PEDOT shells are formed around the silica spheres. Repetitive centrifugation and re-dispersion is performed after the polymerization to remove possible side reactants as well as unreacted chemicals. The process leads to *ca.* 100 mL of a stable colloid with dark blue/grey color depending on the doping level. A final step involved the removal of the silica core by treating the PEDOT-coated silica spheres with 20 wt.% of HF solution to produce hollow PEDOT spheres.

Fig. 1a presents a TEM micrograph of the PEDOT coated silica particles. The coated particles have a shell with a thickness of 5–15 nm. Fig. 1b presents the coated particles after they had been treated with hydrofluoric acid. With the removal of the core, the shell collapsed into a disk with a diameter of *ca.* 140 nm and thickness of *ca.* 80 nm, which is clearly evidenced in Fig. 1b. The decreased dimensions of the shell and the observed disk-like characteristics relative to the coated particles is attributed to the loss of the reinforcing core, clearly absent in Fig. 1b, coupled with the centrifugation and washing of the particles. The formation of the PEDOT shell on the silica was confirmed by FT-IR spectroscopy by observing a C=C vibrational bands at 1365 cm^{-1}, which is due to the quinoidal structure of the thiophene ring,[11] in addition to the strong peak at 470, 801, and 1111 cm^{-1}, which are attributable to the Si–O of silica.[12] After the coated particles have been treated with HF to remove the cores does the FTIR spectrum appear to confirm the presence of the PEDOT shells and the vibrational bands associated with PEDOT which are routinely seen at frequencies of 1600 cm^{-1} and lower are observed[11](C–O–C stretching from ethylene dioxy group at 1242 cm^{-1} and 1080 cm^{-1}, C–S stretching at 700 cm^{-1}, and vibrational bands due to quinoidal structure of the thiophene ring at 1454 and 1365 cm^{-1}).

Fig. 2a presents the UV-Vis transmission spectrum of the PEDOT-coated silica particles randomly dispersed in water. The absorption at 789 nm is due to polaronic or bipolaronic absorption from the PEDOT shell.[10] Taking the coated particles and repeatedly washing them with deionized water and centrifuging them resulted in the particles exhibiting an opalescence. This opalescence was attributed to the self-assembly of the coated

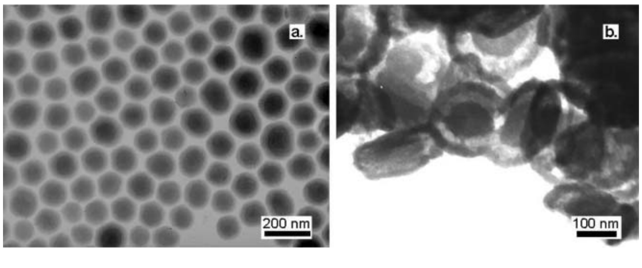

Fig. 1 Transmission electron micrographs of (a) poly (3,4-ethylenedioxythiophene) (PEDOT) coated silica particles and (b) corresponding hollow PEDOT shells after the cores had been removed.

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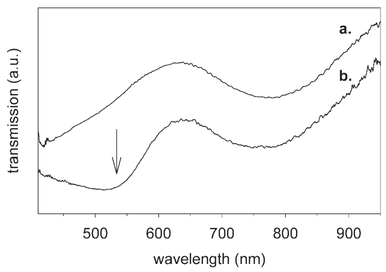


Fig. 2 Transmission spectra of PEDOT-coated silica particles (a) randomly dispersed in water and (b) self-assembled into a crystalline colloidal array. Arrow indicates position of stop band; curves shifted for clarity.

particles into a crystalline colloidal array,[13] where the the dip in the spectrum centered at *ca.* 520 nm (*cf.* Fig. 2b) is due to the creation of a stop band. In addition, in Fig. 2b, the absorption of PEDOT is still clearly discernable in the spectrum. The zeta-potential of the particles was -62.5 mV at a pH of 6.8, indicating that the origin of the self-assembly is due to a negative surface charge.

Fig. 3a presents the reflection characteristics of an opalescent sample at various particle densities, with the most dilute sample exhibiting a reflection peak at *ca.* 610 nm and the most concentrated sample exhibiting a peak at *ca.* 400 nm. This reduction in peak position is attributed to the decreased interparticle spacing and corresponding stop band wavelength, with increased particle concentration.[14] The sensitivity of the stop band position with particle concentration suggests that the self-assembly of the particles was driven through the long-range electrostatic interactions between the surface charges on the particles. When the colloidal solution had a high particle density of *ca.* 30 w/w silica content, the color of the solution was violet (*cf.* Fig. 3b). Adding deionized water resulted in the color of the sample exhibiting radiation of longer wavelengths, transitioning from blue, green, red and finally back to grey-blue or dark blue, the intrinsic color of doped PEDOT. Clearly the intrinsic absorption of the doped PEDOT, coupled with the Bragg diffraction of the crystalline colloidal array, allows for a wide range of accessible colors of the PEDOT-based solution. Unfortunately, attempts to form a crystalline colloidal array with the hollow particles were unsuccessful. This deficiency was largely attributed to the lack of rigidity and uniformity in shape of the particles after the reinforcing cores were removed.

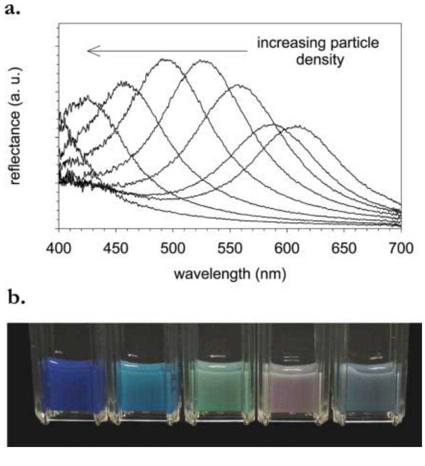
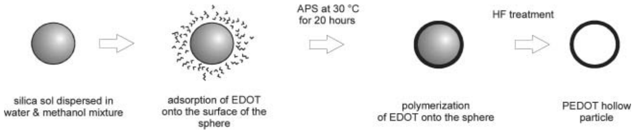


Fig. 3 (a) Reflective characteristics at normal incidence of poly (3,4-ethylenedioxythiophene) (PEDOT) coated silica particles at various particle densities assembled into a crystalline colloidal array and (b) observed colors at various particle densities (from the left: 8.5 × 10^{13} cm^{-3}, 6.4 × 10^{13} cm^{-3}, 4.1 × 10^{13} cm^{-3}, 2.8 × 10^{13} cm^{-3}, while the last sample has a particle density of 2.8 × 10^{13} cm^{-3}, though the opalescence has been destroyed with the addition of a small quantity of NaCl).



Scheme 1 Schematic illustration of the procedure for generating PEDOT-silica core–shell particles and PEDOT hollow particles.

In summary, we have successfully produced nanometre-sized PEDOT-silica core–shell particles and their corresponding hollow particles. The electrostatic interaction between surface charges on the coated particles resulted in their self-assembly into crystalline colloidal arrays with a reflection peak in the visible region. A systematic color change of the colloidal solution could be controlled through the concentration of the coated particles in the medium. The coupling of the intrinsic color of the doped PEDOT with Bragg diffraction may allow for the development of novel color-tunable PEDOT-based opto-electronic devices.

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